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DECOMPOSITION OF HYDRAZINE TO AMMONIA IN PICKERING NGS-A LAY-UP SOLUTION

Report No 91-1-K

P. McSweeney
Chemist
Corrosion Chemistry Section
Chemical Research Department

ABSTRACT

A laboratory study is described to investigate the cause of the rapid decomposition of hydrazine to ammonia observed in Pickering NGS-A lay-up solutions during the retubing of reactors U1 and U2. The effects of the presence of deposits, soluble metal ions, and carbon steel and Monel 400 surfaces were studied under both nitrogen cover and simulated air inleakage conditions. Two conditions accelerated the rate of generation of ammonia: the presence of a substantial area of carbon steel, and low pH in the presence of deposits and oxygen. The rates of generation of ammonia and depletion of hydrazine were insufficient to account for the rapid reactions observed in Pickering lay-up solutions. While a previous study showed anaerobic microorganisms do not survive in the anoxic lay-up solution, no data was available on microorganism growth in the boiler deposit phase.

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EXECUTIVE SUMMARY

DECOMPOSITION OF HYDRAZINE TO AMMONIA IN PICKERING NGS - A LAY-UP SOLUTION

P. McSweeney

A study was undertaken to determine the cause of the rapid decomposition of hydrazine to ammonia in boiler lay-up solution during the retubing of reactors U1 and U2 at Pickering NGS-A. Tests were carried out to simulate boiler lay-up conditions using nitrogen, and 1% and 2% oxygen with balance nitrogen, as cover gases. Tests lasted two to three weeks, and the solutions were agitated to promote or accelerate chemical reactions. Fossil fuelled boiler deposit of a composition similar to Pickering boiler deposits was used in the tests. The effects of the presence of copper and iron oxides, of substantial areas of carbon steel and Monel 400, of high and low pH, and of the presence of soluble iron, copper and nickel ions, were evaluated.

Neither steam generator deposits, copper oxides, iron oxides, Monel 400, nor the presence of soluble metal ions, had a significant effect on the rates of decomposition of hydrazine and generation of ammonia.

The presence of carbon steel resulted in production of ammonia under both nitrogen and nitrogen/oxygen cover gases. The maximum rate of generation of ammonia was 230 mg/L/y. Depression of the pH to 5.0 - 5.5 with sulphuric acid in the presence of deposits and 2% oxygen cover caused ammonia generation at the rate of 450 mg/L/y. These rates of ammonia formation were insufficient to cause the high concentrations of ammonia observed in Pickering lay-up solution. In addition, different from what was observed at Pickering NGS-A, the rate of generation of ammonia did not increase with time.

Corrosion of carbon steel coupons in the solutions was insignificant except under the condition of rapid agitation under 2% O_2 cover in the presence of deposits. No corrosion of Monel 400 coupons was detected.

An earlier microbiological test at Research indicated that anaerobic bacteria do not survive under the anoxic conditions of the lay-up solution. It is recommended that microbial growth within the deposit phase also be studied.

P.S.

job	file	date	report no.
36-614-053	836.333	June 27, 1991	91-1-K

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To Mr. R.W. Patterson
Manager, Chemistry and Metallurgy
CPSD

DECOMPOSITION OF HYDRAZINE TO AMMONIA IN PICKERING NGS-A LAY-UP SOLUTION

P. McSweeney

1.0 INTRODUCTION

During the retubing of reactors U1 and U2 at Pickering NGS-A, the boilers were laid up with a solution of catalyzed hydrazine under nitrogen cover gas. The hydrazine was stable, as expected, during the early stages of the lay-up. After several weeks of lay-up however, it became evident that the hydrazine was decomposing to ammonia at a rate that appeared to increase with time/1/. After several months of lay-up the decay half-life of the hydrazine was less than one day, and the concentration of ammonia in the solution exceeded 1000 mg/L. In an effort to maintain oxygen scavenger in the solution, the hydrazine specification for Unit 2 was revised from the original 75 mg/L to 200 mg/L N_2H_4 as an interim measure. Because of the buildup of ammonia however, the specification was reduced to 50 mg/L hydrazine later during the lay-up.

Attempts at site to increase the half-life of the hydrazine and prevent the buildup of ammonia such as by eliminating air inleakage, and by heating the system to destroy microorganisms, were unsuccessful.

Literature evidence, as well as preliminary work at Research, indicated that the decomposition of hydrazine to ammonia can be accelerated by ions normally present in boiler deposits such as copper and iron ions, and by the presence of oxygen and steel/2,3,4/. A laboratory parametric study was undertaken to determine the effects of conditions, such as the presence of deposits and metal surfaces, to which the Pickering lay-up solutions were exposed, on the rates of decomposition of hydrazine and generation of ammonia. The study is described in this report.

2.0 EXPERIMENTAL

2.1 Equipment

A loop was assembled consisting of four 4-litre covered Pyrex vessels, a solution recirculating pump and associated valves and piping. The system was sealed sufficiently to maintain the dissolved oxygen concentration of nitrogen-covered water in the solvents at < 5 µg/L. Dissolved oxygen was determined using an on-line Orbisphere Model 2110 oxygen sensor. Samples for chemical analysis were obtained by withdrawing aliquots of recirculating solution.

2.2 Overview of Tests

To prepare a test, 4 litres of water in each vessel was sparged with the cover gas prescribed for the test to equilibrate the solution with the gas. Three types of cover gas were evaluated: nitrogen, 1% O_2 balance nitrogen, and 2% O_2 balance nitrogen. For comparison, air inleakages to the Pickering boilers during lay-up usually resulted in 0.5% O_2 in the nitrogen cover gas/1/. Additives were then introduced to simulate the SG environment, approximately 100 mg/L catalyzed hydrazine was added and the gas supply was switched to the blanket mode to commence the test. Most tests lasted two to three weeks.

Samples of solutions were taken two or three times per week and analyzed for pH, hydrazine, ammonia, and dissolved metals believed to be present, by standard analytic techniques. Samples for ammonia and hydrazine determination were preserved with hydrochloric acid solution. Whenever the hydrazine concentration decreased to about 50 mg/L it was made up to approximately 100 mg/L.

A list of additives used to simulate the laid-up steam generator internal environment is shown is Table 1. Two phases of tests are identified in the table. In Phase 1, the solutions were agitated slowly and the sludge concentration was 5 g/L. Since significant decomposition of hydrazine was not observed in the Phase 1 tests, rapid agitation and a higher concentration of sludge were applied in Phase 2 in an attempt to promote chemical reactions. The pH of the solutions was usually 9.0-9.5, but one test at high pH, and one at low pH, were performed in Phase 2. At Pickering, the pH of the solution was in the range 9.2-10.9. All tests were carried out at ambient temperature - approximately 23°C.

The sludge used in the tests consisted of thermal plant steam generator deposits spiked with $CaCO_3$, $CaSO_4$, and $CaSiO_3$ to achieve the composition shown in Table 2. This material is a reasonable simulation of Pickering steam generator deposits/5/.

The addition of iron, copper and nickel sulphates in Phase 1 was an attempt to ensure the presence of soluble metals. However, most of the metals remained undissolved at the pH of the test solution. The carbon steel and Monel 400 surface areas were achieved by the addition of metal filings of known surface area.

2.3 Corrosion Assessment

Corrosion coupons of SA-516 carbon steel and Monel 400 tubing were suspended in the test solutions. The steel coupons measured 5 x 2 x 0.5 cm and were polished to 320 grit. The Monel coupons were 2 cm long. The coupons were rinsed in methanol and weighed before use. They were again rinsed and weighed after use. Some carbon steel coupons contained traces of adherent deposit after use. These coupons were cleaned with Clark's solution, and an appropriate correction factor was applied to compensate for the minor weight loss in Clark's solution. The average corrosion loss was calculated for each coupon, and the coupons were examined for corrosion damage using a stereomicroscope.

3.0 RESULTS

The results of Phase 1 tests, employing slow agitation, are shown in Tables 3.1 through 3.24. Also indicated are the decay half-lives of hydrazine, the rate of increase in ammonia concentrations, and corrosion of carbon steel.

The results for Phase 2, employing rapid agitation, are shown in Tables 4.1 through 4.8. The 1% O_2 cover gas was not evaluated in Phase 2.

Table 5 provides an overview of the effects of test parameters on the half-life of hydrazine.

4.0 DISCUSSION OF RESULTS

4.1 Phase 1

The pH of the test solutions varied because of the additives used, but the pH conformed to the range 9.0-11.0 specified for the Pickering boilers/1/.

The low dissolved oxygen concentrations under nitrogen cover confirmed the system was air-tight. Hydrazine appeared to undergo chemical reactions with the sludge, possibly by reducing oxidized metals, resulting in shorter half-lifes than when sludge was absent (Tables 3.3, 3.5). The concentration of dissolved oxygen was also low under 1% oxygen cover except, apparently, when metal sulphates were added (Tables 3.14, 3.15), when slightly higher concentrations occurred. The cause of the increased oxygen concentration in the presence of added metals is not known.

The concentrations of dissolved iron, copper and nickel were low under all test conditions.

The additives had no significant effect on the rate of decomposition of hydrazine. The shortest half-life (16d, Table 3.19) occurred under 2% O_2 cover.

The presence of carbon steel caused a noticeable increase in the rate of production of ammonia. The maximum rate was 230 mg/L/y (Table 3.18), but the rate of production did not increase with

time, different from what was observed in Pickering boilers.

The rate of corrosion of carbon steel in the solutions was negligible. No corrosion of Monel 400 was observed.

4.2 Phase 2

The dissolved oxygen concentrations in Phase 2 were similar to those in Phase 1 for the corresponding cover gas.

Dissolved copper was detected in all tests containing either sludge or copper oxides. Iron and nickel were detected under 2% oxygen, particularly at low pH.

The half-life of hydrazine was frequently shorter than observed in Phase 1. Under nitrogen cover, there was no evidence of ammonia being produced in the presence of either sludge, copper oxides or iron oxides. Trace ammonia was produced under 2% oxygen cover in the presence of sludge and copper oxides. Elevation of the pH to 10.2-10.9 (Table 4.8) did not enhance the production of ammonia. While metal ions may catalyze decomposition of hydrazine under some conditions, the results indicate that iron, copper and nickel ions were not responsible for the rapid conversion of hydrazine to ammonia in Pickering boilers. Although the duration of the tests was only 2 to 3 weeks compared with the Pickering lay-up period of several months, it is not believed longer tests would have resulted in a different finding.

Significant concentrations of ammonia were observed at low pH in the presence of sludge under 2% oxygen (Table 4.7). A similar observation was reported previously at Research Division/4/. However, the rate of generation of ammonia (450 mg/L/y) was too low to account for the high concentrations of ammonia observed in Pickering boilers. In addition, there was no indication that the rate of generation of ammonia increased with time, different from what occurred in Pickering lay-up solution. The data in Table 4.7 show that the hydrazine that was not converted to ammonia was stable at low pH.

The presence of sludge, combined with the rapid stirring, caused noticeable corrosion of carbon steel even in the absence of oxygen (Table 4.1). Particles of sludge adhered to the carbon steel surfaces apparently because of the rapid stirring, and it was at these sites that most of the corrosion occurred. No corrosion of Monel 400 was detected.

5.0 BIOLOGICALLY INDUCED EFFECTS

The study indicated that the presence of deposits, metal surfaces and oxygen do not accelerate the rate of production of ammonia sufficiently to account for the rapid formation of ammonia observed in Pickering boilers. This finding highlights the possibility that microbial growth within the lay-up solution may have been responsible for the build-up of ammonia. In an effort to kill microorganisms that may have been in the generators, they were drained and refilled with 80°C water/6/. Subsequent lay-up of the generators showed little evidence of a reduction in the rate

of generation of ammonia. However, this does not prove that microorganisms did not exist in the generators because some bacteria can survive at 80°C. A microbiological test to determine the presence of anoxic bacteria was conducted at Research/7/, using a sample of lay-up solution from a Pickering generator. Bacteria were not detected in the solution. Despite this result, it is possible that microbial growth occurred at deposit surfaces in the generators/8/, causing conversion of hydrazine to ammonia. No deposit was available for testing however. Further tests are recommended to study microbial growth in lay-up solution in the presence of steam generator deposits.

6.0 CONCLUSIONS

Bench scale parametric tests were conducted to study the cause of the rapid decomposition of hydrazine to ammonia in Pickering-A boiler lay-up solutions during the retubing of U1 and U2. Nitrogen, and 1% and 2% oxygen with balance nitrogen were the cover gases in the tests.

Neither steam generator deposits, copper oxides, iron oxides, Monel 400, nor copper, iron and nickel in soluble form had a significant effect on the rates of decomposition of hydrazine and generation of ammonia.

The presence of carbon steel caused production of ammonia in the solutions. The maximum rate of production due to carbon steel was 230 mg/L/y. Depression of the pH to 5.0-5.5 with sulphuric acid, in the presence of deposits and 2% O_2 cover, resulted in ammonia generation at the rate of 450 mg/L/y. These rates of generation of ammonia are not believed to be sufficient to cause the high concentration of ammonia observed in Pickering boilers. Different from what was observed at Pickering, the rate of generation of ammonia did not increase with time.

Corrosion of carbon steel was minimal during slow agitation. During rapid agitation the presence of sludge, the corrosion rate of carbon steel was high because of adhesion of sludge to the coupon surfaces. No corrosion of Monel 400 was detected.

An earlier microbiological test at Research indicated that the anaerobic bacteria do not survive in the bulk lay-up solution. The effects of steam generator deposits on microbial growth were not studied however. It is recommended that microbial growth within the deposit phase, and its possible effects on the stability of hydrazine, be also studied.

Approved by:

D.J.R. Dodd
Manager
Chemical Research Department

Submitted by:

P. McSweeney
Chemist
Corrosion Chemistry Section

Reviewed by:

P. Spekkens
Section Head
Corrosion Chemistry Section

PMcS:dmc:cmf

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TABLE 1

LIST OF ADDITIVES

Additive	Concentration
Phase 1, Slow Agitation	
Sludge	5 g/L
$FeSO_4$	3 mg/L Fe
$NiSO_4$	3 mg/L Ni
$CuSO_4$	3 mg/L Cu
Carbon Steel	200 cm^2/L
Monel 400	400 cm^2/L
Phase 2, Rapid Agitation	
Sludge	15 g/L
Fe_3O_4 (powder)	15 g/L
Fe_2O_3 (powder)	15 g/L
$CuO + Cu_2O$ (1:1 mixture)	15 g/L
NaOH solution	to pH 10.5-11.0
H_2SO_4 solution	to pH 5.3-5.5

Note: In Pickering boilers, carbon steel $\simeq$ 100 cm^2/L, Monel $\simeq$ 1300 cm^2/L

TABLE 2

COMPOSITION OF SLUDGE

	g/kg
Fe	183
Cu	192
Ni	34
Zn	6
Si	53
Ca	161
SO_4	37
P	< 1
Major phases identified	Fe_3O_4, Cu
Minor phases identified	Fe_2O_3, CuO

TABLE 3.1

PHASE 1, N_2 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
4	9.3	2	102	0.2	<0.05	<0.05	<0.05	
6	9.2	2	97	0.2				
8	9.3	4	82	0.3	<0.05	<0.05	<0.05	
11	9.3	2	93	0.2				
13	9.4	3	87	0.3				
15	9.3	2	85	0.3	<0.05	<0.05	<0.05	Ca = 72 mg/L

Approximate half-life of N_2H_4: 33d
Rate of production of NH_3: <10 µg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.2

PHASE 1, N_2 200 cm^3/L CS

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
1	9.6	1	114	0.3	<0.05
2	9.5	1	114	0.5	<0.05
4	9.4	1	113	1.0	<0.05
9	9.6	2	111	1.9	<0.05
11	9.5	1	106	3.7	<0.05
15	9.6	2	106	4.9	<0.05
18	9.3	2	103	5.9	<0.05
21	9.4	3	98	7.1	<0.05

Approximate half-life of N_2H_4: 71d
Rate of production of NH_3: 124 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.3
PHASE 1, N_2 200 cm^2/L CS, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species					Remarks
		DO µg/L	mg/L				
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.5	1	112	0.3	<0.05	<0.05	<0.05	
2	9.5	1	105	0.5				
4	9.4	1	104	0.7	<0.05	<0.05	<0.05	
9	9.4	5	97	1.6				
11	9.4	2	94	2.7				
15	9.4	1	90	3.5	<0.05	<0.05	<0.05	Ca = 56mg/L
18	9.5	1	85	4.0				
21	9.6	2	73	4.0	<0.05	<0.05	<0.05	Ca = 53 mg/L

Approximate half-life of N_2H_4: 29d
Rate of production of NH_3: 68 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.4
PHASE 1, N_2 400 cm^2/L MONEL

Days Elapsed	pH	Concentration Dissolved Species				
		DO µg/L	mg/L			
			N_2H_4	NH_3	Cu	Ni
1	9.6	1	114	0.1	<0.05	<0.05
2	9.5	2	113	0.1		
4	9.4	3	113	0.2	<0.05	<0.05
9	9.4	2	114	0.6		
11	9.5	1	114	1.0		
15	9.5	2	113	1.5	<0.05	<0.05
18	9.5	2	108	1.7		
21	9.6	3	101	1.7	<0.05	<0.05

Approximate half-life of N_2H_4: 89d
Rate of production of NH_3: 29 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.5

PHASE 1, N_2 400 cm^2/L MONEL, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.6	1	110	0.1	<0.05	0.1	<0.05	
2	9.5	1	108	0.2				
4	9.3	4	101	0.3				
9	9.3	2	95	0.4	<0.05	<0.05	<0.05	
11	9.2	2	97	0.4				
15	9.4	3	91	0.5	<0.05	<0.05	<0.05	Ca = 56 mg/L
18	9.3	2	84	0.5				
21	9.4	2	80	0.5	<0.05	<0.05	<0.05	Ca = 53 mg/L

Approximate half-life of N_2H_4: 37d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.6

PHASE 1, N_2 3 mg/L Fe^{2+}

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
4	9.2	3	111	0.6	
6	9.2	4	110	0.6	<0.05
8	9.1	2	111	0.6	0.07
11	9.2	3	110	0.6	0.06
13	9.1	2	108	0.6	0.1
15	9.0	1	108	0.6	0.2

Approximate half-life of N_2H_4: >100d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.7

PHASE 1, N_2 3 mg/L Cu^{2+}

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Cu
4	9.2	4	104	0.7	0.16
6	9.2	1	103	0.6	0.12
8	9.3	1	104	0.5	0.11
11	9.2	2	104	0.5	
13	9.2	1	98	0.5	0.14
15	9.2	1	99	0.4	0.10

Approximate half-life of N_2H_4: >100d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.8

PHASE 1, N_2, NO ADDITION

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
4	9.6	6	109	0.3	<0.05
6	9.7	4	109	0.3	
8	9.6	4	106	0.3	
11	9.7	4	106	0.3	<0.05
13	9.6	3	106	0.3	
15	9.6	3	106	0.3	<0.05

Approximate half-life of N_2H_4: >100d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.9

PHASE 1, 1% O_2, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.4	3	95	0.7	<0.05	<0.05	<0.05	
3	9.3	5	94	0.6				
7	9.2	7	85	0.6				
8	9.3	7	81		<0.05	<0.05	<0.05	
10	9.2	6	78	0.7				
13	9.2	6	74	0.7				
15	9.2	4	63	0.8	0.1	<0.05	<0.05	Ca = 70 mg/L

Approximate half-life of N_2H_4: 20d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 4 µm/y

TABLE 3.10

PHASE 1, 1% O_2, 200 cm^2/L CS

Days Elapsed	pH	Concentration Dissolved Species				Remarks
		DO µg/L	mg/L			
			N_2H_4	NH_3	Fe	
1	9.5	5	101	0.9	<0.05	
3	9.7	9	101	1.6		
6	9.5	5	101	2.3		
10	9.6	16	96		<0.05	NH_3 not analyzed

Approximate half-life of N_2H_4: 100d
Rate of production of NH_3: 56 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.11

PHASE 1, 1% 0_2, 200 cm^2/L CS, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species					
		DO µg/L	mg/L				
			N_2H_4	NH_3	Fe	Cu	Ni
1	9.4	2	96	1.2	<0.05	<0.05	<0.05
3	9.4	3	94	1.7	<0.05	0.08	<0.05
6	9.5	3	90	2.2			
10	9.4	6	78	3.0			

Approximate half-life of N_2H_4: 24d
Rate of production of NH_3: 70 mg/L/y
CS Corrosion: Average loss <2µm/y

TABLE 3.12

PHASE 1, 1% 0_2, 400 cm^2/L MONEL

Days Elapsed	pH	Concentration Dissolved Species				
		DO µg/L	mg/L			
			N_2H_4	NH_3	Cu	Ni
1	9.5	2	101	0.6	0.08	<0.05
3	9.7	4	101	0.6		
6	9.5	7	100	0.6	0.08	<0.05
10	9.7	10	96	0.7		

Approximate half-life of N_2H_4: 90d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2µm/y

TABLE 3.13

PHASE 1, 1% 0_2, 400 cm^2/L MONEL, 5g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species					
		DO µg/L	mg/L				
			N_2H_4	NH_3	Fe	Cu	Ni
1	9.5	2	95	1.0			
3	9.4	4	94	0.6	<0.05	0.1	<0.05
6	9.4	4	90	0.8			
10	9.3	11	77	1.0	<0.05	<0.05	<0.05

Approximate half-life of N_2H_4: 23d
Rate of production of NH_3: <10 mg/L/y

TABLE 3.14

PHASE 1, 1% 0_2, 3 mg/L Fe^{2+}, 3 mg/L Ni^{2+}

Days Elapsed	pH	Concentration Dissolved Species				
		DO µg/L	mg/L			
			N_2H_4	NH_3	Fe	Ni
1	9.0	23	102	0.5	<0.05	<0.05
3	9.0	20	101	0.4		
7	9.0	11	99	0.4	<0.05	<0.05
8	9.0	14	97	0.4		
10	9.1	25	97	0.4	0.1	<0.05
13	9.0	31	94	0.6	<0.05	<0.05
15	9.1	40	94	0.6	<0.05	<0.05

Approximate half-life of N_2H_4: 90d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 6 µm/L/y

TABLE 3.15

PHASE 1, 1% 0_2, 3 mg/L Cu^{2+}

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Cu
1	9.3	5	103	0.8	0.1
3	9.3	9	104	0.8	0.1
7	9.2	15	100	0.7	0.1
8	9.2	22	97	0.8	0.1
10	9.3	16	95	0.7	0.1
13	9.3	21	94	1.0	0.2
15	9.2	14	92	1.0	0.2

Approximate half-life of N_2H_4: 65d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 4 µm/y

TABLE 3.16

PHASE 1, 1% 0_2, No Addition

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
1	9.3		103	0.4	
3	9.6	4	100	0.6	<0.05
7	9.4	6	97	0.5	
8	9.4	8	94	0.5	
10	9.4	11	94	0.6	<0.05
13	0.5	7	91	0.8	
15	9.4	15	90	0.7	<0.05

Approximate half-life of N_2H_4: 55d
Rate of production of NH_3: <10 µm/y
CS Corrosion: Average loss 3µm/y

TABLE 3.17
PHASE 1, 2% 0_2, 5g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.3	11	79	1.7				
2	9.2		74					
5	9.2	67	70	1.9	<0.05	<0.05	<0.05	Ca = 64 mg/L
7	9.2	49	72	2.1				
9	9.3	13	61	2.1	<0.05	<0.05	<0.05	
9			121					After N_2H_4 make-up
12	9.3	71	102	2.3				
16	9.2	20	93	2.3				
19	9.2	23	88	2.7	<0.05	<0.05	<0.05	
21	9.2	37	75	3.0				Ca = 72 mg/L

Approximate half-life of N_2H_4: 17d
Rate of production of NH_3: 24 mg/L/y
CS Corrosion: Average loss 4 µm/y

TABLE 3.18
PHASE 1, 2% 0_2, 200 cm^2/L CS

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
1	9.5	15	95	0.4	<0.05
4	9.5	10	93	3.5	
6	9.6	45	92	4.9	<0.05
8	9.5	48	84	7.4	
11	9.5	48	84	7.4	
13	9.6	43	80	8.3	<0.05
15	9.7	50	78	9.4	<0.05

Approximate half-life of N_2H_4: 40d
Rate of production of NH_3: 230 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.19

PHASE 1, 2% 0_2, 200 cm^2/L CS, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.2	5	93	1.0	<0.05	<0.05	<0.05	
4	9.4	23	88	1.6				
6	9.3	20	81	2.3				
8	9.4	27	77	2.8	<0.05	<0.05	<0.05	Ca = 77 mg/L
11	9.5	33	74	3.4				
13	9.6	63	53	4.4				
15	9.6	122	52	4.4	<0.05	<0.05	<0.05	

Approximate half-life of N_2H_4: 16d
Rate of production of NH_3: 89 mg/L/y
CS Corrosion: Average loss 3 µm/y

TABLE 3.20

PHASE 1, 2% 0_2, 400 cm^2 MONEL

Days Elapsed	pH	Concentration Dissolved Species				
		DO µg/L	mg/L			
			N_2H_4	NH_3	Cu	Ni
1	9.3	15	102	0.5		
4	9.2	34	95	0.5	<0.05	<0.05
6	9.2	27	95	0.5		
8	9.4	76	94	0.5		
11	9.4	149	94	0.5	<0.05	<0.05
13	9.4	134	89	0.6		
15	9.5	130	89	0.6	<0.05	<0.05

Approximate half-life of N_2H_4: 55d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 3.21

PHASE 1, 2% 0_2, 400 cm^2/L MONEL, 5 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
1	9.3	41	96	0.7				
4	9.3	70	91	0.7	<0.05	<0.05	<0.05	
6	9.2	15	83	0.8				
8	9.3	16	82	0.9				
11	9.3	73	79	0.9	<0.05	<0.05	<0.05	Ca = 77 mg/L
13	9.3	67	69	1.1				
15	9.3	124	67	1.1	<0.05	<0.05	<0.05	

Approximate half-life of N_2H_4: 23d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 3 µm/y

TABLE 3.22

PHASE 1, 2% 0_2, 3 mg/L Fe^{2+} + 3 mg/L Ni^{2+}

Days Elapsed	pH	Concentration Dissolved Species					
		DO µg/L	mg/L				
			N_2H_4	NH_3	Fe	Cu	Ni
1	8.9	60	98	0.3			
2			98	0.3	<0.05	<0.05	<0.05
5	8.9	69	93	0.3			
7	8.9	77	91	0.4			
9	8.9	67	89	0.4	<0.05	<0.05	<0.05
12	9.0	71	85	0.5			
16	8.9	76	76	0.5	<0.05	<0.05	<0.05

Approximate half-life of N_2H_4: 33d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 18µm/y; trace general corrosion

TABLE 3.23

PHASE 1, 2% 0_2, 3 mg/L Cu^{2+}

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Cu
1	9.2	20	90	0.6	<0.05
2	9.1	20	89	0.7	
5	9.1	19	88	0.8	
7	9.1	36	88	0.8	<0.05
9	9.1	27	84	0.9	
12	9.1	66	78	1.0	<0.05
16	9.2	22	71	1.1	<0.05

Approximate half-life of N_2H_4: 35d
Rate of production of NH_3: 10 mg/L/y
CS Corrosion: Average loss 11 µm/y

TABLE 3.24

PHASE 1, 2% 0_2, NO ADDITION

Days Elapsed	pH	Concentration Dissolved Species				Remarks
		DO µg/L	mg/L			
			N_2H_4	NH_3	Fe	
1	9.4	30	93	0.1		
2	9.4	25	88	0.1	<0.05	
5	9.4	37	85	0.1		
7	9.3	37	82	0.2		
9	9.3	38	78	0.2	<0.05	
9			116			After N_2H_4 make-up
12	9.4	50	109	0.3		
16	9.3	48	100	0.4	<0.05	

Approximate half-life of N_2H_4: 25d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 4.1
PHASE 2, N_2, 15 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
START	9.2	7	109	0.5				
3	9.1	1	81	0.5				
5	9.1	3	70	0.6	<0.05	0.3	<0.05	Ca = 212 mg/L
7	9.1	5	63	0.7				
7	9.4		109					After N_2H_4 make-up
10	9.2	3	95	0.8	<0.05	0.2	<0.05	Ca = 216 mg/L
12	9.2	5	93	0.7				
17	9.2	2	88	0.7	<0.05	0.2	<0.05	Ca = 216 mg/L

Approximate half-life of N_2H_4: 8d before make-up, 26d after make-up
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 96 µm/y; general corrosion

TABLE 4.2
PHASE 2, N_2, 15 g/L Fe_20_3

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
START	9.1	6	108		
3	9.0	1	105	0.8	
5	8.9	8	105	0.5	<0.05
7	9.0	1	105	0.6	
10	9.1	3	104	0.6	<0.05
12	9.0	10	102	0.9	
17	9.0	3	102	0.9	<0.05

Approximate half-life of N_2H_4: >100d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 6 µm/y

TABLE 4.3

PHASE 2, N_2, 15g/L Fe_3O_4

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Fe
START	9.8	2	106		
3	9.8	1	103	0.4	
5	9.8	1	102	0.5	<0.05
7	9.8	1	101	0.4	
10	9.9	2	100	0.5	<0.05
12	9.8	3	100	0.5	
17	9.8	5	100	0.5	<0.05

Approximate half-life of N_2H_4: >100d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 3 µm/y

TABLE 4.4

PHASE 2, N_2, 7.5 g/L CuO + 7.5 g/L Cu_2O

Days Elapsed	pH	Concentration Dissolved Species			
		DO µg/L	mg/L		
			N_2H_4	NH_3	Cu
START	9.0	4	105		
3	8.9	1	87	0.7	0.6
5	8.9	1	78	0.7	
7	8.9	1	71	0.7	0.2
10	8.8	1	58	0.7	
12	8.8	2	46	0.7	0.3
17	8.7	2	29	0.7	0.1

Approximate half-life of N_2H_4: 10d
Rate of production of NH_3: <10 mg/L/y
CS Corrosion: Average loss 3µm/y

TABLE 4.5
PHASE 2, 2% 0_2, 15 g/L SLUDGE

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
START			100					
1	8.8	41	75	0.3	1.3	0.30	0.16	
3	8.5	43	42	1.0				
3			95					After N_2H_4 make-up
6	8.5	45	60	1.3	0.12	0.50	<0.05	
6			100					After N_2H_4 make-up
8	8.5	41	44	1.4				
10	8.5	43	36	1.6	<0.05	0.36	<0.05	
10			110					After N_2H_4 make-up
13	8.6	51	105		0.07	0.10	0.06	
15			84	2.5	<0.05	1.6	0.09	

Approximate half-life of N_2H_4: Varied from 3 to 11 days
Rate of production of NH_3: 54 mg/L/y
CS Corrosion: Average loss 218 µm/y; shallow pitting, general corrosion

TABLE 4.6
PHASE 2, 2% 0_2, 7.5 g/L Cu0 + 7.5 g/L Cu_20

Days Elapsed	pH	Concentration Dissolved Species				Remarks
		DO µg/L	mg/L			
			N_2H_4	NH_3	Cu	
1	9.3	40	95	0.3		
3	9.1	28	86	0.3		
6	9.0	28	38	0.4	1.0	
6			107			After N_2H_4 make-up
8	9.0	44	98	0.5	1.0	
10	9.1	51	78	0.5		
13	9.1	48	48	0.7	0.36	
15	9.1	49	30	1.1	0.9	

Approximate half-life of N_2H_4: 5d
Rate of production of NH_3: 21 mg/L/y
CS Corrosion: Average loss <2 µm/y

TABLE 4.7
PHASE 2, 2% 0_2, 15 g/L SLUDGE, pH 5.0-5.5

Days Elapsed	pH	Concentration Dissolved Species					
		DO µg/L	mg/L				
			N_2H_4	NH_3	Fe	Cu	Ni
1	5.5	38	86	0.8	26	0.08	1.8
3	5.5	42	74	1.3			
6	5.3	43	71	4.3	58	0.23	1.3
8	5.4	39	71	6.1			
10	5.4	42	65	8.5	52	0.20	0.20
13	5.6	39	63	14.0			
15	5.5	43	63	17.9	49	0.20	0.8

Approximate half-life of N_2H_4: 25d
Rate of production of NH_3: 450 mg/L/y
CS Corrosion: Average loss 530 µm/y; extensive general corrosion and pitting

TABLE 4.8
PHASE 2, 2% 0_2, 15 g/L SLUDGE, pH 10.8-11.0

Days Elapsed	pH	Concentration Dissolved Species						Remarks
		DO µg/L	mg/L					
			N_2H_4	NH_3	Fe	Cu	Ni	
START	10.9		100					
1	10.5	32	85	0.2	<0.05	0.05	<0.05	Add NaOH to pH 10.9
3	10.8	29	25	0.3	0.3	5.0	0.06	
3			105					After N_2H_4 make-up
6		46	15	0.3	1.0	80	1.0	
6			101					After N_2H_4 make-up
8	10.8	40	90	0.4				
10	10.8	42	66	0.4	4.3	22	0.9	
10			100					After N_2H_4 make-up
13	10.8	42	65	0.5	1.0	19	0.13	
15	10.9	42	41	0.9	0.10	0.5	0.8	

Approximate half-life of N_2H_4: 2-4d
Rate of production of NH_3: 18 mg/L/y
CS Corrosion: Average loss 310 µm/y; general corrosion

TABLE 5

SUMMARY OF EFFECTS OF TEST CONDITIONS ON N_2H_4 HALF-LIFE

TABLE	STIRRING	SLUDGE	CS	MONEL	METAL IONS	COVER	pH	N_2H_4 HALF-LIFE
	Slow Rapid	Yes/No				Nitrogen 1%O_2 2%O_2	Normal Low High	Days
3.1	S	Y	N	N	N	N	N	33
3.2	S	N	Y	N	N	N	N	71
3.3	S	Y	Y	N	N	N	N	29
3.4	S	N	N	Y	N	N	N	89
3.5	S	Y	N	Y	N	N	N	37
3.6	S	N	N	N	Fe^{2+}	N	N	>100
3.7	S	N	N	N	Cu^{2+}	N	N	>100
3.8	S	N	N	N	N	N	N	>100
3.9	S	Y	N	N	N	1%	N	20
3.10	S	N	Y	N	N	1%	N	100
3.11	S	Y	Y	N	N	1%	N	24
3.12	S	N	N	Y	N	1%	N	90
3.13	S	Y	N	Y	N	1%	N	23
3.14	S	N	N	N	Ni^{2+},Fe^{2+}	1%	N	90
3.15	S	N	N	N	CU^{2+}	1%	N	65
3.16	S	N	N	N	N	1%	N	55
3.17	S	Y	N	N	N	2%	N	17
3.18	S	N	Y	N	N	2%	N	40
3.19	S	Y	Y	N	N	2%	N	16
3.20	S	N	N	Y	N	2%	N	55
3.21	S	Y	N	Y	N	2%	N	23
3.22	S	N	N	N	Ni^{2+}, Fe^{2+}	2%	N	33
3.23	S	N	N	N	Cu^{2+}	2%	N	35
3.24	S	N	N	N	N	2%	N	25
4.1	R	Y	N	N	N	N	N	8,26
4.2	R	Fe_2O_3	N	N	N	N	N	>100
4.3	R	Fe_3O_4	N	N	N	N	N	>100
4.4	R	CuO+Cu_2O	N	N	N	N	N	10
4.5	R	Y	N	N	N	2%	N	3-11
4.6	R	CuO+Cu_2O	N	N	N	2%	N	5
4.7	R	Y	N	N	N	2%	L	25
4.8	R	Y	N	N	N	2%	H	2-4